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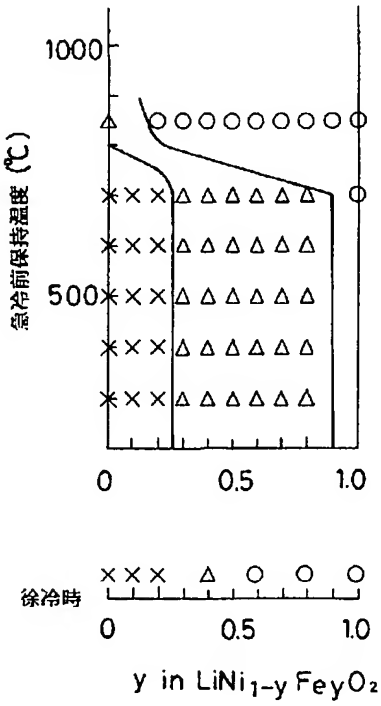
(54)【発明の名称】　電極材料の合成法

(57)【要約】

【目的】　本発明は、リチウム二次電池の正極材料として優れた特性を有する六方晶の結晶構造を有する$Li_xNi_{1-y}M_yO_2$（MはＣｏ、Ｆｅ、Ｍｎ、Ｃｒ、Ｖ、Ｔｉ）で表される電極材料の合成法を提供する。

【構成】　コバルトイオン、鉄イオン、マンガンイオン、クロムイオン、バナジウムイオン、チタンイオンを含む化合物より選ばれる一種類あるいは複数の化合物とリチウム酸化物、ニッケル酸化物を混合し、前記混合体を加熱反応させ、その後該反応生成物が六方晶の結晶構造をとる温度より急冷する。



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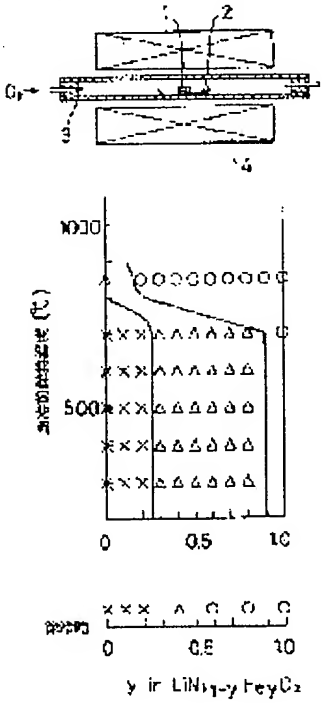
(54) SYNTHESIS OF ELECTRODE MATERIAL



(57)Abstract:
PURPOSE: To perform the synthesis of the electrode material, which is expressed by LixNi1-yMyO2 (M represents, Co, Fe, Mn, Cr, V, Ti) having the hexagonal crystal structure, which has the excellent characteristic as the positive electrode material for a lithium secondary battery.
CONSTITUTION: One kind or multiple kinds of the compounds selected among the compounds, which include cobalt ion, iron ion, manganese ion, chrome ion, vanadium ion, titanium ion, is/are mixed with lithium oxide and nickel oxide, and this mixture is heated for reaction, and thereafter, it is cooled quickly from the temperature for forming the reaction product into the hexagonal crystal structure. At the time of heating the mixture, an annular furnace 4, in which a tablet 1 of the mixture is placed on an alumina boat 2 and this boat 2 is put in an alumina core tube 3 filled with the inside oxygen gas, is heated to a predetermined temperature.

CLAIMS

[Claim(s)]
[Claim 1] Cobalt ion, iron ion, manganese ion, chromium ion, vanadium ion, One kind, or two or more compounds and lithium oxides chosen from the compound containing titanium ion, Lix nickel1-y My O2 (it Co(es) M) to which a nickel oxide is mixed, the pyrogenetic reaction of said mixture is carried out, and this resultant is characterized by quenching from the temperature which takes the hexagonal crystal structure after that The synthesis method of an electrode material expressed with one kind or two or more metals which are chosen from Fe, Mn, Cr, V, and Ti.
[Claim 2] The synthesis method of the electrode material according to claim 1 characterized by the electrode material expressed with Lix nickel1-y My O2 (one kind or two or more metals with which M is chosen from Co, Fe, Mn, Cr, V, and Ti) fulfilling the conditions of $y< 0.3$.
[Claim 3] Claim 1 to which the compound containing cobalt ion, iron ion, manganese ion, chromium ion, vanadium ion, and titanium ion is characterized by being cobalt oxide, a ferric acid ghost, a manganic acid ghost, a chromic-acid ghost, a banazin san ghost, and a titanic-acid ghost, or the synthesis method of an electrode material according to claim 2.
[Claim 4] a ferric acid ghost -- iron oxide (III) (Fe 2O3) it is -- synthesis method of the electrode material according to claim 3 characterized by things.
[Claim 5] The synthesis method of the electrode material according to claim 4 characterized by the quenching initiation temperature of a mixture being below 700-degreeC.
[Claim 6] The synthesis method of an electrode material given in claim 1 thru/or any of 5 they are. [which is characterized by for lithium oxide being a peroxidation lithium (I) and (Li 2O2), and nickel oxides being nickel oxide (II) and (NiO)]
[Claim 7] The synthesis method of an electrode material given in claim 1 thru/or any of 6 they are. [which is characterized by calcinating a mixture under an oxygen ambient atmosphere]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the synthesis method of the electrode material used as positive active material of a lithium cell.
[0002]
[Description of the Prior Art] In recent years, with development of portable devices, such as a personal computer and a cellular phone, since a lithium cell can obtain a high energy consistency as a power source, research is done briskly [every direction].
[0003] Here, as the electrode material used for the above lithium cells, especially an electrode material used for a lithium secondary battery, many researches on the matter

which has the layer structure or three-dimension network structure of a transition-metals oxide or a transition-metals sulfide are made. When these matter is used as an electrode material, the electrochemical reaction turns into a topochemical reaction called the intercalation day intercalation reaction of the electrochemical lithium ion to the empty site in a crystal lattice. The reversibility of such a topochemical reaction has many outstanding things, and the lithium secondary battery using such matter as an electrode material shows the outstanding charge-and-discharge cycle property.

[0004] It has such the two-dimensional layer structure, and the nickel oxide which is transition-metals oxide, manganese oxide, cobalt oxide, etc. are mentioned to the empty site in the crystal lattice as matter in which the electrochemical intercalation day intercalation reaction of a lithium ion is possible. Lix NiO2 which contained the lithium beforehand in nickel oxide and cobalt oxide, and LiCoO2 It compounds and what was replaced with Spinel structure is known as that example by drawing out a lithium electrochemically from this ingredient.

[0005] It is LiNiO2 by carrying out heating fusion of nickel oxide and the lithium oxide, and cooling to a room temperature, when using nickel oxide as positive active material. It compounds. Lix NiO2 which has the crystal structure of NaCl structure by deintercalating a lithium ion from the compound ingredient electrochemically Lix nickel 2O4 A spinel is obtained. It is Lix NiO2 especially. A cubic and a hexagonal crystalline form are taken and a thing (ordered NaCl mold) with order nature and the thing (disordered NaCl mold) which is not exist in this cubic further. It can use preferably from a stratified compound hexagonal as positive active material of a cell producing the intercalation day intercalation reaction of a lithium ion smoothly.

[0006] Furthermore, the intercalation day intercalation reaction of a lithium ion can be made to perform in the higher potential range more smoothly by permuting a part of nickel in this crystal structure by Co, Fe, Mn, Cr, V, Ti, etc.

[0007]

[Problem(s) to be Solved by the Invention] For example, although the synthesis method which mixes and calcinates lithium oxide, nickel oxide, and an iron oxide, and is annealed in a furnace is taken when compounding what permuted a part of nickel by Fe, since the cubic crystal structure is thermally stable in the range in which the amount of permutations of Fe exceeds 30% of nickel, the thermal equilibrium state at the time of annealing is LiNi1-y Fey O2 of a cubic [be / hexagonal]. It will be in a mixture condition. Therefore, cubic LiNi1-y Fey O2 intermingled in the ingredient when this ingredient was used as an electrode material In order not to act as an active material, it had the technical problem that it became what has a small cell capacity.

[0008] This invention solves a technical problem above and aims at offering the synthesis method of the electrode material which has the property which was excellent as a positive-electrode ingredient of a lithium secondary battery.

[0009]

[Means for Solving the Problem] Cobalt ion, iron ion, manganese ion, chromium ion, vanadium ion, Mix one kind, or two or more compounds and the lithium oxide chosen from the compound containing titanium ion, and a nickel oxide, carry out the pyrogenetic reaction of said mixture, and this resultant after that by quenching from the temperature which takes the hexagonal crystal structure The electrode material expressed with Lix nickel1-y My O2 (one kind or two or more metals with which M is chosen from Co, Fe,

Mn, Cr, V, and Ti) is compounded.
[0010] In addition, as for the electrode material expressed with Lix nickel1-y My O2 (one kind or two or more metals with which M is chosen from Co, Fe, Mn, Cr, V, and Ti), what fulfills the conditions of y< 0.3 is desirable.
[0011] Moreover, as a compound containing cobalt ion, iron ion, manganese ion, chromium ion, vanadium ion, and titanium ion, it is desirable to use cobalt oxide, a ferric acid ghost, a manganic acid ghost, a chromic-acid ghost, a banazin san ghost, and a titanic-acid ghost.
[0012] Moreover, it is desirable to use iron(III) oxide (Fe 2O3) as a ferric acid ghost, and, as for the initiation temperature of quenching of a mixture, carrying out to below 700-degreeC is still more desirable.
[0013] Moreover, it is desirable to use nickel oxide (II) and (NiO) as a nickel oxide, using a peroxidation lithium (I) and (Li 2O2) as lithium oxide.
[0014] Moreover, it is desirable to perform baking of a mixture under an oxygen ambient atmosphere.
[0015]
[Function] y takes the crystal structure of hot and a cubic in the small range, and Lix nickel1-y My O2 (one kind or two or more metals with which M is chosen from Co, Fe, Mn, Cr, V, and Ti) takes the hexagonal crystal structure at low temperature. (For example, the case 2, i.e., LiNi1-y Fey O, of M=Fe In the temperature requirement of T>=800-degreeC, it is ordered. A NaCl mold or disordered All of a NaCl mold take the crystal structure of ******, and it is ordered in the temperature requirement of T<=700-degreeC depending on the presentation. The hexagonal crystal structure of a NaCl mold is taken.) If these crystal structures are quenched to a room temperature, they will be in the so-called "condition that the crystal structure in a pyrosphere was frozen", and will maintain the structure before cooling. Therefore, after holding a sample at the temperature which takes hexagonal structure, the electrode material in which the property which could obtain the sample in which a cubic is not intermingled and was excellent also in the room temperature as positive active material of a lithium cell quenching to a room temperature is shown can be obtained. Moreover, also when it changes into Fe and Co, Mn, Cr, V, and Ti are used, the electrode material which has the hexagonal crystal structure similarly can be obtained.
[0016] Moreover, Lix nickel1-y My O2 Since the hexagonal crystal structure arises in the range of y< 0.3 as presentation range, this presentation range is used especially more preferably.
[0017] Moreover, since the starting material at the time of permuting some nickel ion by cobalt ion, iron ion, manganese ion, chromium ion, vanadium ion, and titanium ion tends to obtain oxide as a product, cobalt oxide, a ferric acid ghost, a manganic acid ghost, a chromic-acid ghost, a banazin san ghost, and a titanic-acid ghost are used preferably.
[0018] Moreover, as a ferric acid ghost, iron(III) oxide (Fe 2O3) is preferably used in this case, and below 700-degreeC that is the temperature requirement which takes the hexagonal crystal structure as quenching initiation temperature in that case is chosen preferably.
[0019] Moreover, it is preferably used from nickel oxide (II) and (NiO) arising as lithium oxide used as starting material, and it being hard to arise an oxygen deficiency in a product as a peroxidation lithium (I), (Li 2O2), and a nickel oxide.

[0020] Moreover, the bottom of the oxygen ambient atmosphere which an oxygen deficiency similarly cannot produce easily as a firing environments of mixture is desirable.
[0021]
[Example] Hereafter, this invention is explained to a detail using an example.
[0022] (Example 1) Using a peroxidation lithium (I), (Li 2O2), nickel oxide (II) and (NiO), and iron(III) oxide (Fe 2O3) as starting material, it cools with the quenching method by liquid nitrogen, and is LiNi1-y Fey O2. The electrode material expressed was compounded.
[0023] That is, they are Li 2O2, NiO, and Fe 2O3 first. Weighing capacity was carried out by the ratio of mole-ratio 1:1-y:y (0<=y<=1), and it mixed in the alumina mortar. They are 4 ton/cm2 in 0.3g of this mixture. Pressing was carried out to the shape of a tablet of 7mmphi by the pressure. In addition, this weighing capacity, mixing, and pressing were performed inside the glove compartment filled with argon gas.
[0024] Thus, the tablet of the mixture of the obtained start ingredient was put on the boat made from an alumina, was put into the interior into oxygen gas passage ********, carried out the temperature up with the programming rate of 50 degreedegreeC/h to 850-degreeC in the oxygen air current, and was calcinated at the temperature for 48 hours. In addition, although the schematic diagram of a firing furnace is shown in drawing 1 , one is the tablet of mixture among drawing and, as for an alumina boat and 3, 2 is [the reactor core tube of an alumina and 4] tube furnaces. Then, it cooled slowly with the cooling rate of 50-degreeC/h to each temperature of 300-700-degreeC, the alumina boat was taken out after that, and the sample was quenched in liquid nitrogen. Moreover, quenching was performed by the approach more nearly same than the burning temperature of 850-degreeC. It cooled slowly at the rate of 50-degreeC/h to the room temperature after the same baking further again.
[0025] The result of having identified the crystal structure of these samples by powder X-ray diffractometry is shown in drawing 2 . In addition, in drawing 2 , an axis of ordinate shows the retention temperature after 850-degreeC baking, and x, **, and O are ordered respectively. A NaCl mold (hexagonal), disordered A NaCl mold (tetragonal phase), ordered The presentation-temperature by which the diffraction peak which belongs to a NaCl mold (tetragonal phase) was mainly observed is shown.
[0026] It turns out that, as for what was annealed from this result before quenching in [presentation] y< 0.3 to the thing which quenched by the temperature maintenance below 700-degreeC which takes the hexagonal crystal structure, or the room temperature, the thing of the hexagonal crystal structure occupies most. Moreover, it turns out that, as for the thing which quenched from the temperature which takes cubic structure also in [presentation] y< 0.3, or the thing of the presentation range of y>=0.3, the thing of the cubic crystal structure occupies most.
[0027] It investigated by constituting a lithium secondary battery for the electrode characteristic of these samples, and next, measuring the cell property. The detail is given below.
[0028] Graphite was mixed as electronic electric conduction material, carboxymethyl-cellulose 1wt% was mixed with each sample obtained above as binding material 10wt(s)%, and it considered as the positive-electrode ingredient of a lithium cell. Pressing of the 500mg of this positive-electrode ingredient was carried out to the path of

15mmphi, and the positive-electrode pellet was obtained.
[0029] In propylene carbonate, it dissolved and the electrolytic solution prepared lithium perchlorate (LiClO4) so that it might become the concentration of 2M.
[0030] The lithium secondary battery which has a cross section as shown in drawing 3 in a negative electrode using a metal lithium foil with a thickness of 0.24mm, using polypropylene micro porous membrane with a thickness of 50 micrometers as a separator was constituted using these positive-electrode pellets and the electrolytic solution. In addition, for a positive-electrode pellet and 6, as for the electrolytic solution and 8, in drawing 3 , a separator and 7 are [5 / a negative electrode and 9] the battery cases of stainless steel nature.
[0031] In order to investigate the electrode characteristic of a sample, this cell was charged by 1mA constant current. Sample LiNi1-y Fey O2 which used liquid nitrogen for drawing 4 and quenched from 700-degreeC The charging curve which followed the thing of y= 0.1 and y= 0.3 is shown inside. However, it sets to drawing 4 and an axis of abscissa is LiNi1-y Fey O2 by charge. It is Li1-x nickel1-y Fey O2 about the presentation of the positive active material in the deintercalated amount of lithiums, i.e., charge. x values at the time of expressing are shown. Although the day intercalation reaction of the lithium ion from a positive electrode was smoothly performed in charge actuation by the sample of y= 0.1 from this drawing, it turns out by the sample of y= 0.3 that the day intercalation reaction of the lithium ion from a positive electrode was not smoothly performed in charge actuation.
[0032] The charging curve which performed measurement same about that which quenched from 700-degreeC about the thing of y= 0.1, and the thing annealed to the room temperature next is shown in drawing 5 . Although what was annealed is about 80% and charge capacity quenched it compared with that which quenched, it turns out that the property excellent in the direction is shown.
[0033] The result of having performed same actuation about other samples is shown in Table 1. In Table 1, O shows that in which the day intercalation reaction of the smooth lithium ion accompanying charge actuation occurred, i.e., the thing which the day intercalation reaction to x>=0.5 produced, and x shows what did not happen.
[0034]
[Table 1]

y / ℃	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
300	○	○	○	×	×	×	×	×	×	×	×
400	○	○	○	×	×	×	×	×	×	×	×
500	○	○	○	×	×	×	×	×	×	×	×
600	○	○	○	×	×	×	×	×	×	×	×
700	○	○	○	×	×	×	×	×	×	×	×
850	×	×	×	×	×	×	×	×	×	×	×

[0035] Although the day intercalation reaction of a lithium ion has produced that which quenched from the temperature which has a crystal structure more nearly hexagonal than

the result of Table 1 and drawing 2 and it is possible to use as a positive-electrode ingredient of a lithium secondary battery, in the thing of ******, a day intercalation reaction does not arise but it turns out that it cannot use as an active material.
[0036] (Example 2) It is LiNi1-y Fey O2 by the quenching method change into the quenching method by liquid nitrogen, and according to a congruence roller. The electrode material expressed was compounded.
[0037] Li 2O2, NiO, and Fe 2O3 Mixing was performed like the example 1. Pressing of this mixture is carried out to the shape of a tablet, and under an oxygen ambient atmosphere, it reserve-calcinates, cools slowly by 850-degreeC, and is LiNi1-y Fey O2. The constituent was obtained.
[0038] This baking object was ground to the grain size of 50 or less meshes, and it reheated and quenched with the quenching equipment shown in drawing 6 . In addition, among drawing 6 , ten are a feeder, and carry and trickle the preliminary baking object 11 after grinding at the congruence roller 12. Moreover, 13 is the infrared oven, and it is heated so that it may become the temperature of a request of the preliminary baking object 11. Reheating quenching of the preliminary baking object was carried out at various temperature using this quenching equipment.
[0039] Thus, the crystal structure of the obtained sample and the electrode characteristic were performed like the example 1. Consequently, the result as an example 1 with the almost same relation between re-burning temperature, and the crystal structure and the electrode characteristic was obtained.
[0040] (Example 3) As starting material, it cobalt oxide [a peroxidation lithium (I), (Li 2O2), nickel oxide (II) and (NiO), and] (IV) (CoO2) Uses, and is LiNi1-y Coy O2 with the same approach as an example 1. The electrode material expressed was compounded.
[0041] Thus, the crystal structure of the obtained sample and the electrode characteristic were performed like the example 1. Consequently, about the acquired crystal structure, the almost same result as an example 1 was obtained. Moreover, about the electrode characteristic, the potential which a lithium ion deintercalates changed slightly, it is a request and the almost same result as an example 1 was obtained about the electrode characteristic.
[0042] (Example 4) as starting material -- a peroxidation lithium (I), (Li 2O2), nickel oxide (II) and (NiO), and manganese(IV) oxide (MnO2) -- using -- the same approach as an example 2 -- LiNi1-y Mny O2 The electrode material expressed was compounded.
[0043] Thus, the crystal structure of the obtained sample and the electrode characteristic were performed like the example 1. Consequently, about the acquired crystal structure, the almost same result as an example 1 was obtained. Moreover, about the electrode characteristic, the potential which a lithium ion deintercalates changed slightly, it is a request and the almost same result as an example 1 was obtained about the electrode characteristic.
[0044] (Example 5) As starting material, it vanadium oxide [lithium oxide (I), (Li2 O), nickel oxide (II) and (NiO), and] (V) (V2 O5) Uses, and is LiNi1-y Vy O2 with the same approach as an example 1. The electrode material expressed was compounded.
[0045] Thus, the crystal structure of the obtained sample and the electrode characteristic were performed like the example 1. Consequently, about the acquired crystal structure, the almost same result as an example 1 was obtained. Moreover, about the electrode characteristic, the potential which a lithium ion deintercalates changed slightly, it is a

request and the almost same result as an example 1 was obtained about the electrode characteristic.

[0046] (Example 6) as starting material -- a peroxidation lithium (I), (Li 2O2), nickel oxide (II) and (NiO), and chromium(III) oxide (Cr 2O3) -- using -- the same approach as an example 1 -- LiNi1-y Cry O2 The electrode material expressed was compounded.

[0047] Thus, the crystal structure of the obtained sample and the electrode characteristic were performed like the example 1. Consequently, about the acquired crystal structure, the almost same result as an example 1 was obtained. Moreover, about the electrode characteristic, the potential which a lithium ion deintercalates changed slightly, it is a request and the almost same result as an example 1 was obtained about the electrode characteristic.

[0048] (Example 7) As starting material, it titanium oxide [lithium oxide (I), (Li2 O), nickel oxide (II) and (NiO), and] (IV) (TiO2) Uses, and is LiNi1-y Tiy O2 with the same approach as an example 2. The electrode material expressed was compounded.

[0049] Thus, the crystal structure of the obtained sample and the electrode characteristic were performed like the example 1. Consequently, about the acquired crystal structure, the almost same result as an example 1 was obtained. Moreover, about the electrode characteristic, the potential which a lithium ion deintercalates changed slightly, it is a request and the almost same result as an example 1 was obtained about the electrode characteristic.

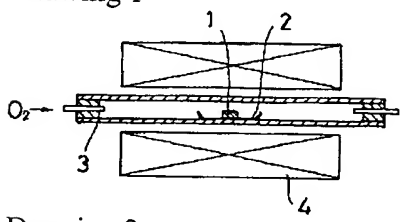
[0050]

[Effect of the Invention] According to this invention, the electrode material which has the property which was excellent as a positive-electrode ingredient of a lithium secondary battery is compoundable as mentioned above.

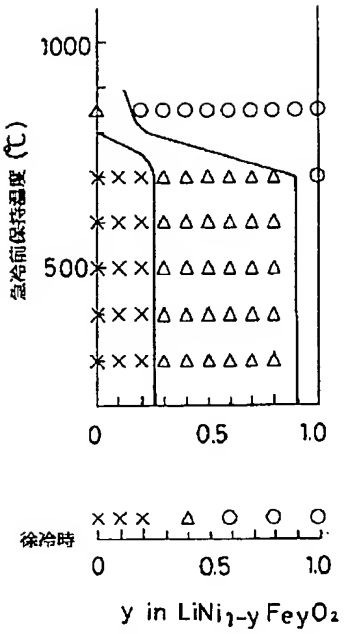
[0051] In addition, to say nothing of [although quenching with an injection into liquid nitrogen and a congruence roller was explained as a quenching method] the same effectiveness being acquired by other approaches, such as an injection into other distilled water and an organic solvent, and spraying of coolant gas, in the example of this invention, this invention is not limited to quenching with an injection into liquid nitrogen, and a congruence roller as a quenching method.

[0052] Moreover, it sets in the example of this invention and is Lix nickel1-y My O2. It cannot be overemphasized that the effectiveness same about other presentations is acquired although only the thing of x= 1.0 was explained as a presentation, either, and this invention is Lix nickel1-y My O2. It is not limited to the thing of x= 1.0 as a presentation.

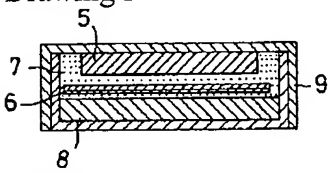
Drawing 1



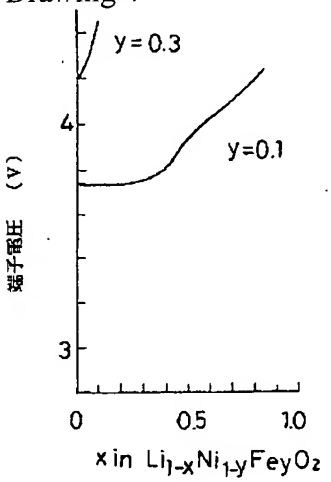
Drawing 2



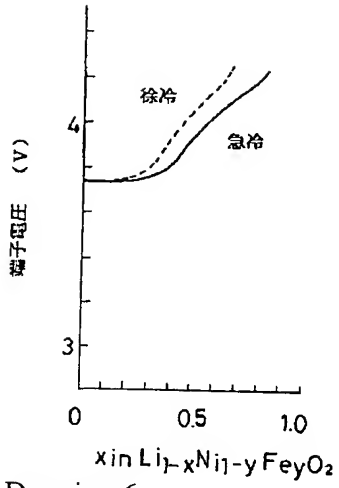
Drawing 3



Drawing 4



Drawing 5



Drawing 6